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Ong et al.

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(54) **ANALYTICAL METHODOLOGY FOR QUALITATIVE AND QUANTITATIVE DETERMINATION OF CHEMICAL AGENT VAPOR**

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(52) **U.S. Cl.** **436/177**; 436/161; 436/171; 436/178; 436/181; 422/68.1; 422/69; 422/88; 422/89; 73/23.41; 73/863.12; 73/1.02

(58) **Field of Search** 73/863.12, 1.03, 73/23.41, 863.11; 436/177, 161, 171, 178, 181; 422/68.1, 69, 88, 89

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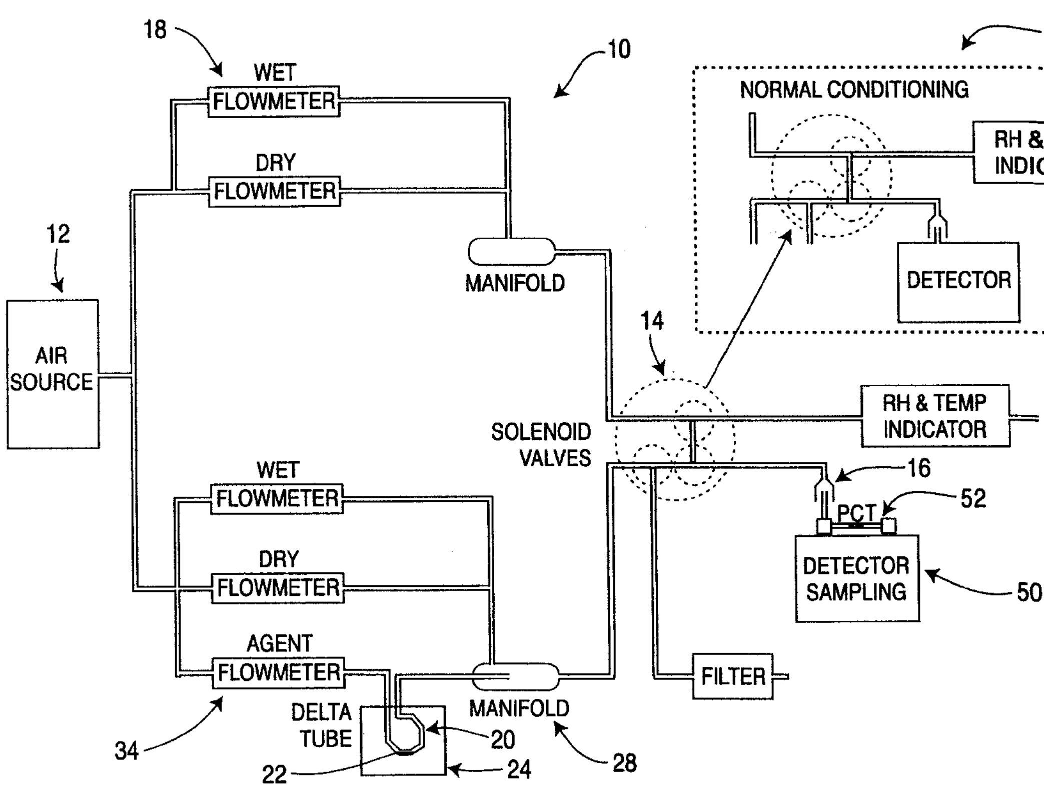
(57) **ABSTRACT**

A method for producing and sampling chemical agent vapor comprising the steps of placing neat chemical agent in a reservoir, purging the chemical agent in the reservoir with a dry air, and analyzing the air stream exiting the reservoir. A MINICAMS having a removable PCT may be used to analyze the air stream exiting the reservoir. The method may further comprise the steps of changing the relative humidity conditions and testing chemical agent detectors.

19 Claims, 6 Drawing Sheets



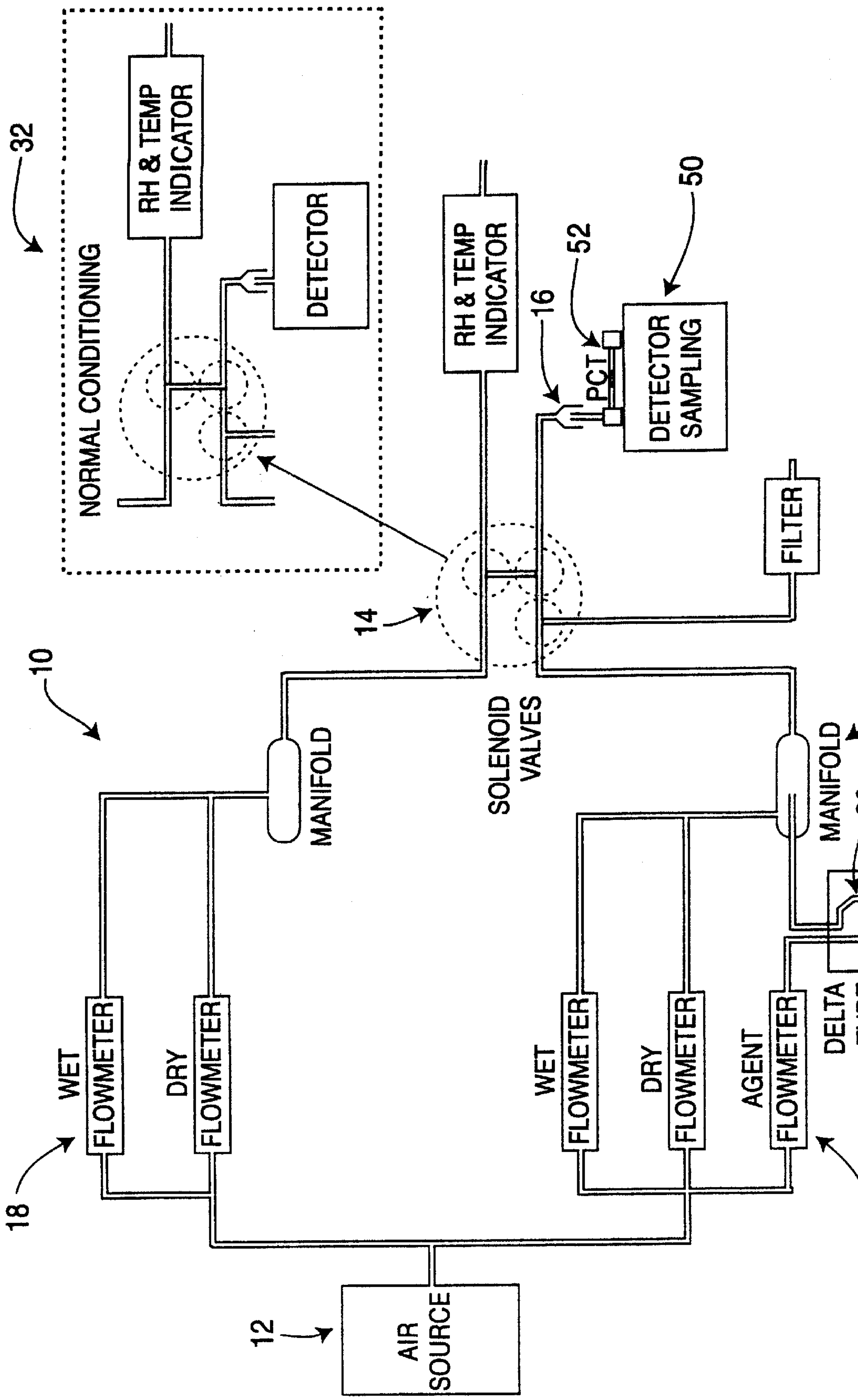

32
NORMAL CONDITIONING
RH & TEMP INDICATOR
DETECTOR
RH & TEMP INDICATOR
16
52
50
PCT
DETECTOR SAMPLING
FILTER
14
10
SOLENOID VALVES
MANIFOLD
28
MANIFOLD
20
24
DELTA TUBE
22
WET FLOWMETER
DRY FLOWMETER
18
WET FLOWMETER
DRY FLOWMETER
AGENT FLOWMETER
34
12
AIR SOURCE

FIG. 1

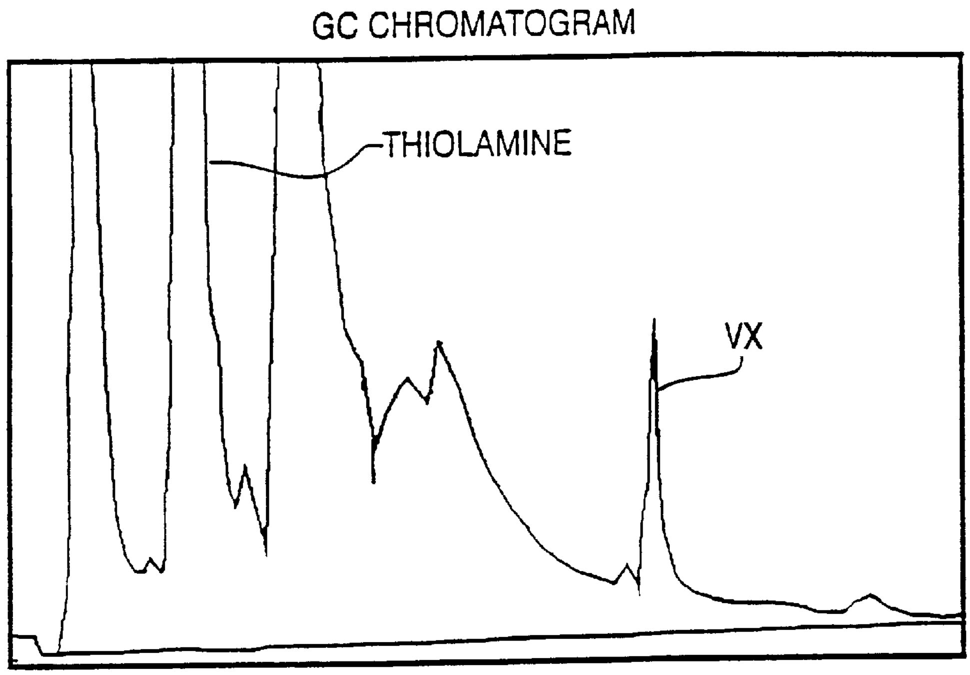

GC CHROMATOGRAM
THIOLAMINE
VX

FIG. 2A

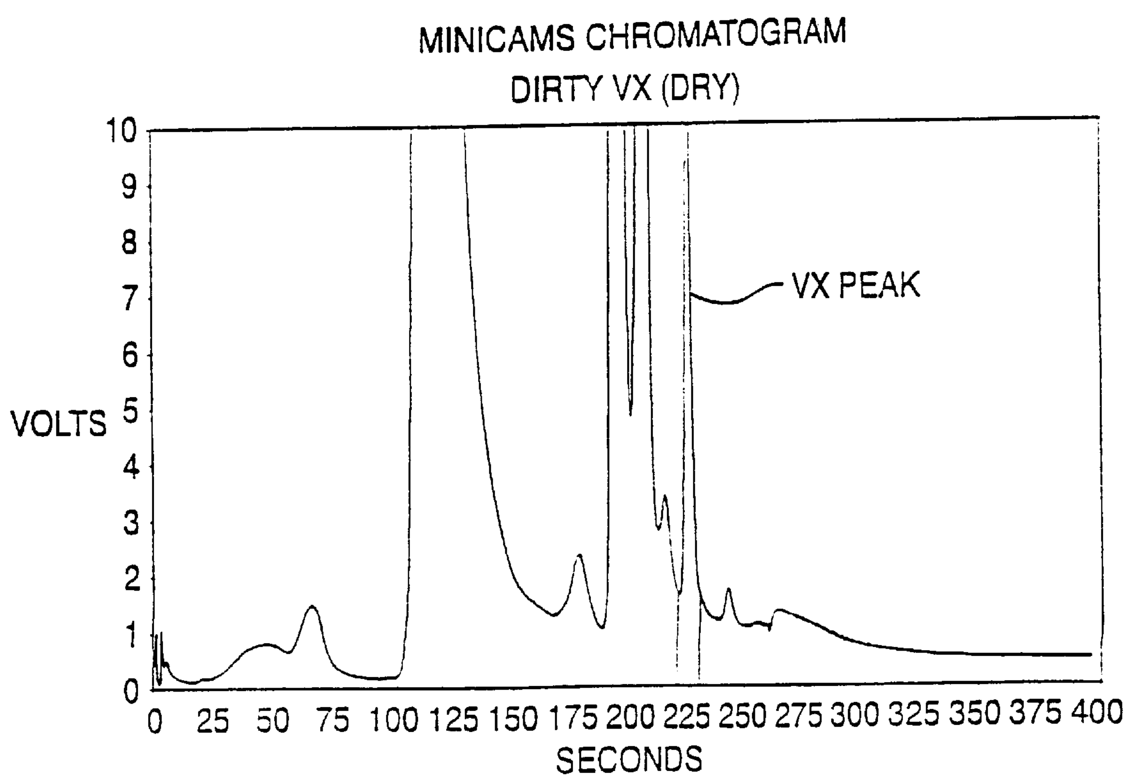

MINICAMS CHROMATOGRAM
DIRTY VX (DRY)
VX PEAK
VOLTS
0
1
2
3
4
5
6
7
8
9
10
0 25 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400
SECONDS

FIG. 2B

GC CHROMATOGRAM

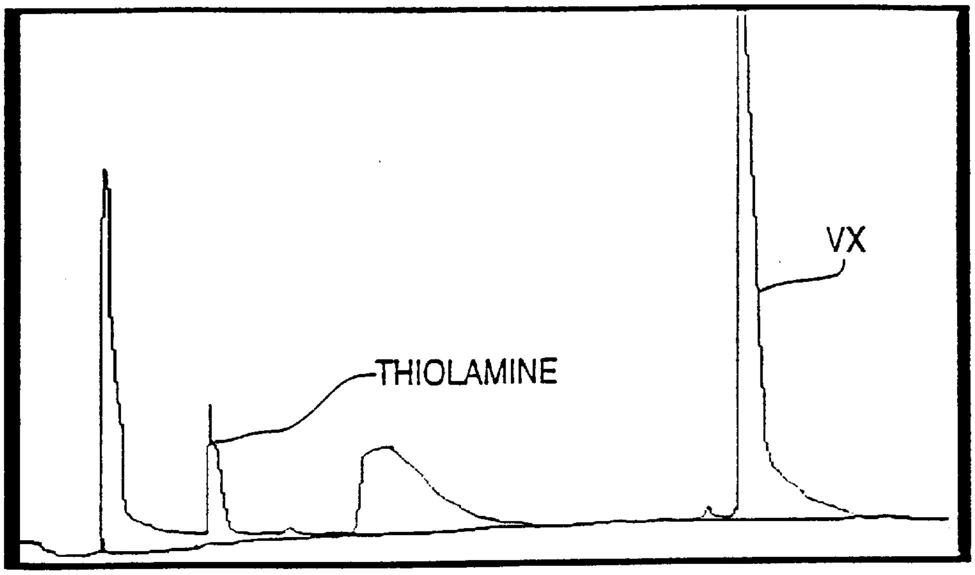


FIG. 3A

MINICAMS CHROMATOGRAM

SEMI-PURE VX SAMPLE

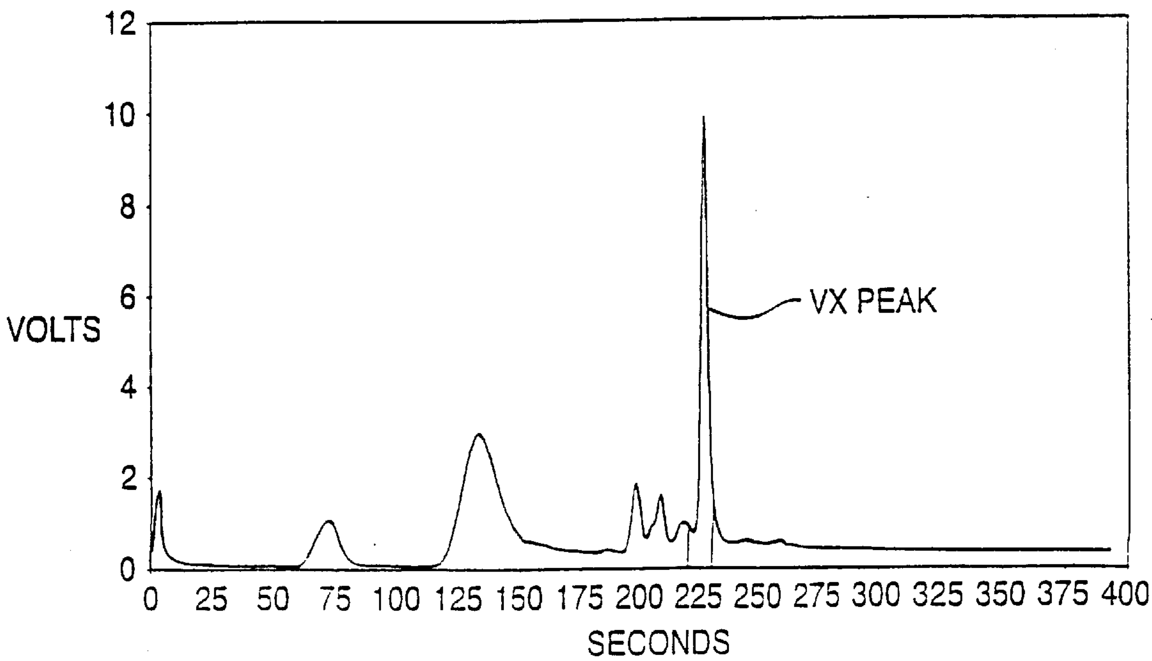


FIG. 3B

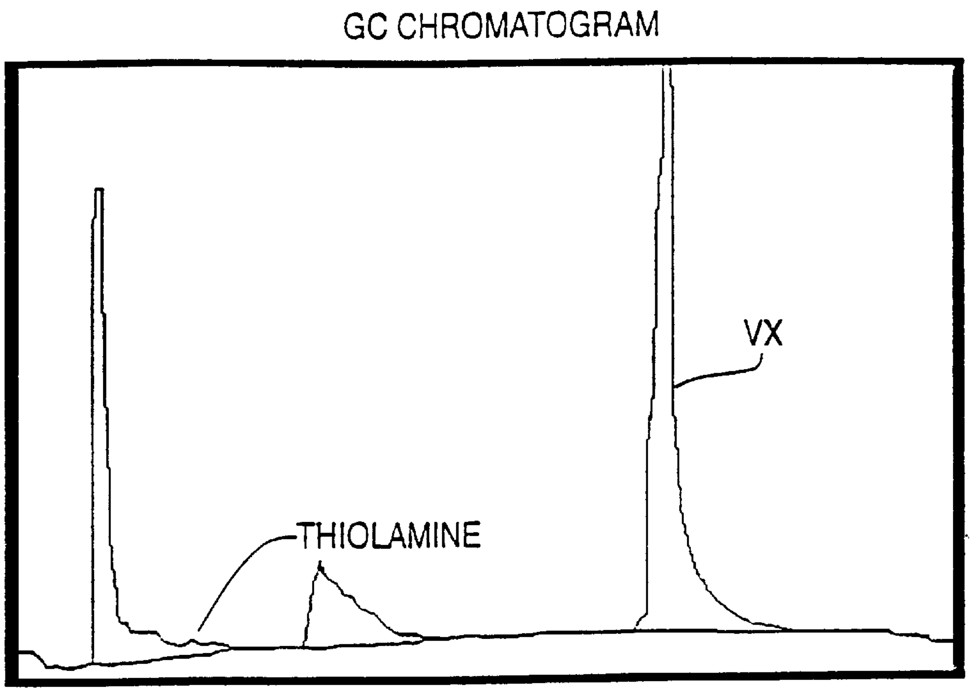

GC CHROMATOGRAM
VX
THIOLAMINE

FIG. 4A

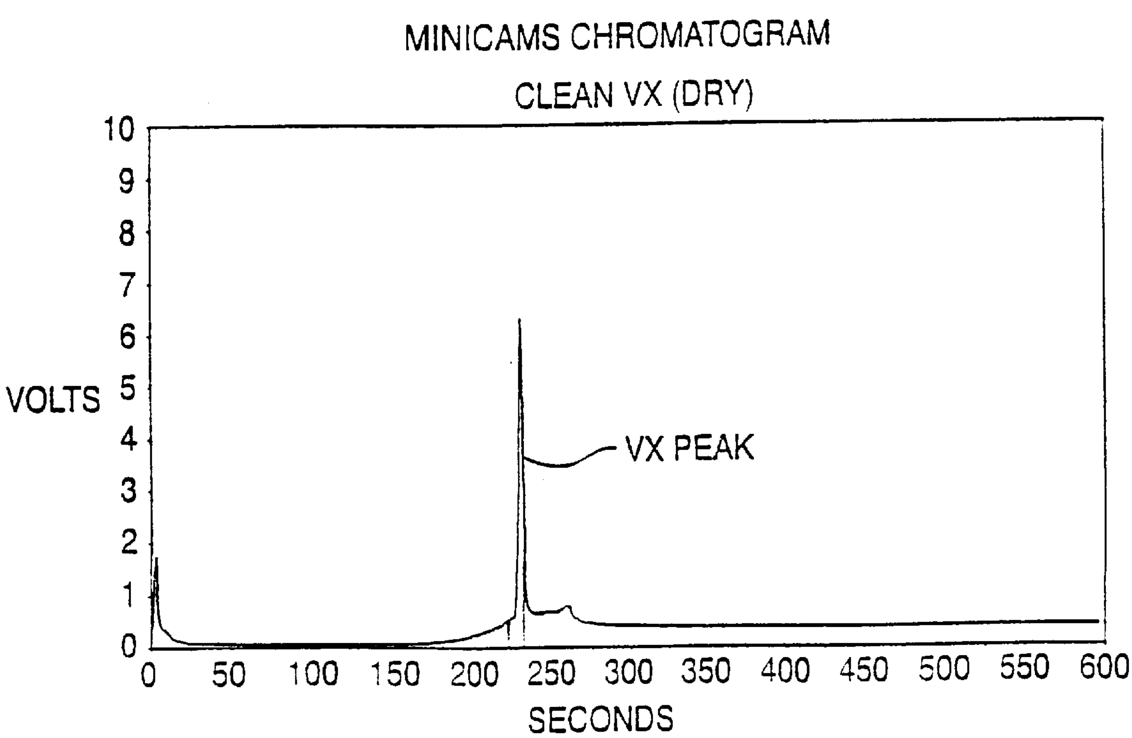

MINICAMS CHROMATOGRAM
CLEAN VX (DRY)
10
9
8
7
6
VOLTS 5
4
3
2
1
0
VX PEAK
0 50 100 150 200 250 300 350 400 450 500 550 600
SECONDS

FIG. 4B

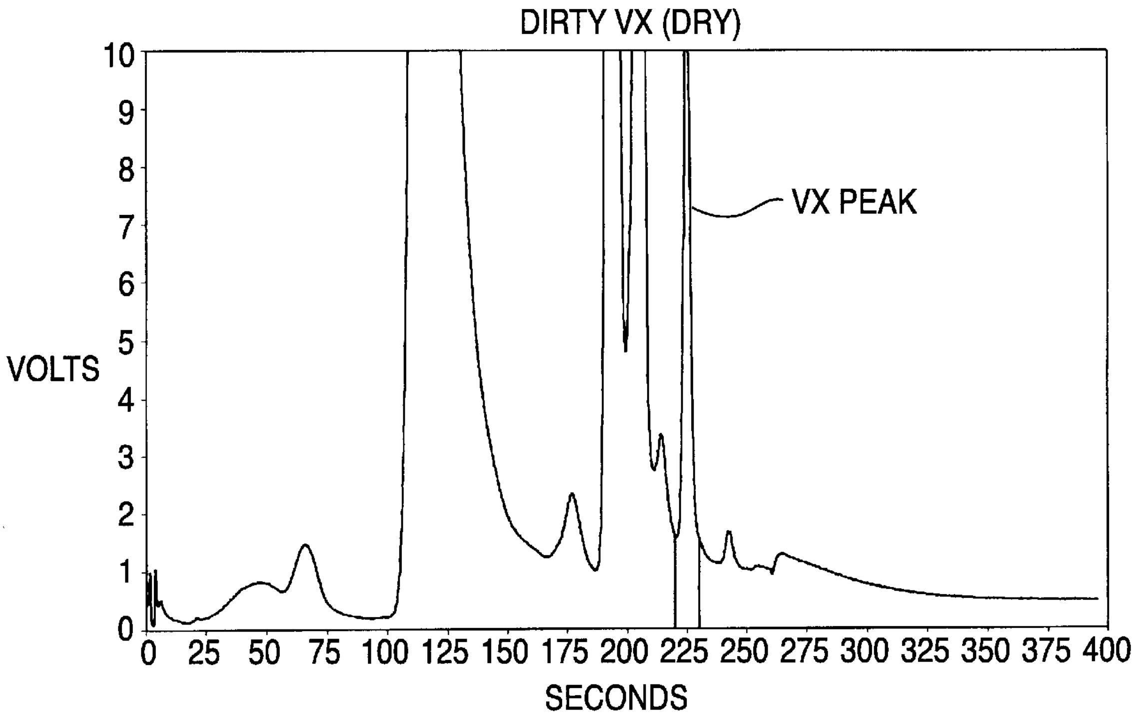

DIRTY VX (DRY)
VOLTS
VX PEAK
0
1
2
3
4
5
6
7
8
9
10
0 25 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400
SECONDS

FIG. 5A

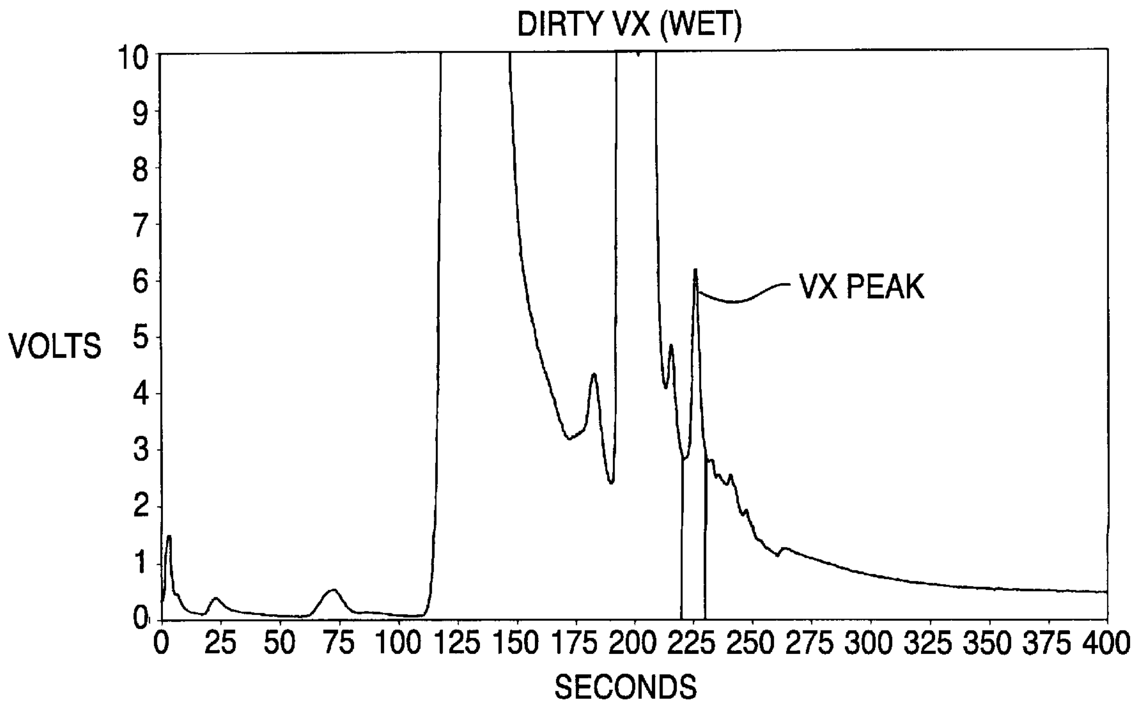

DIRTY VX (WET)
VOLTS
VX PEAK
0
1
2
3
4
5
6
7
8
9
10
0 25 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400
SECONDS

FIG. 5B

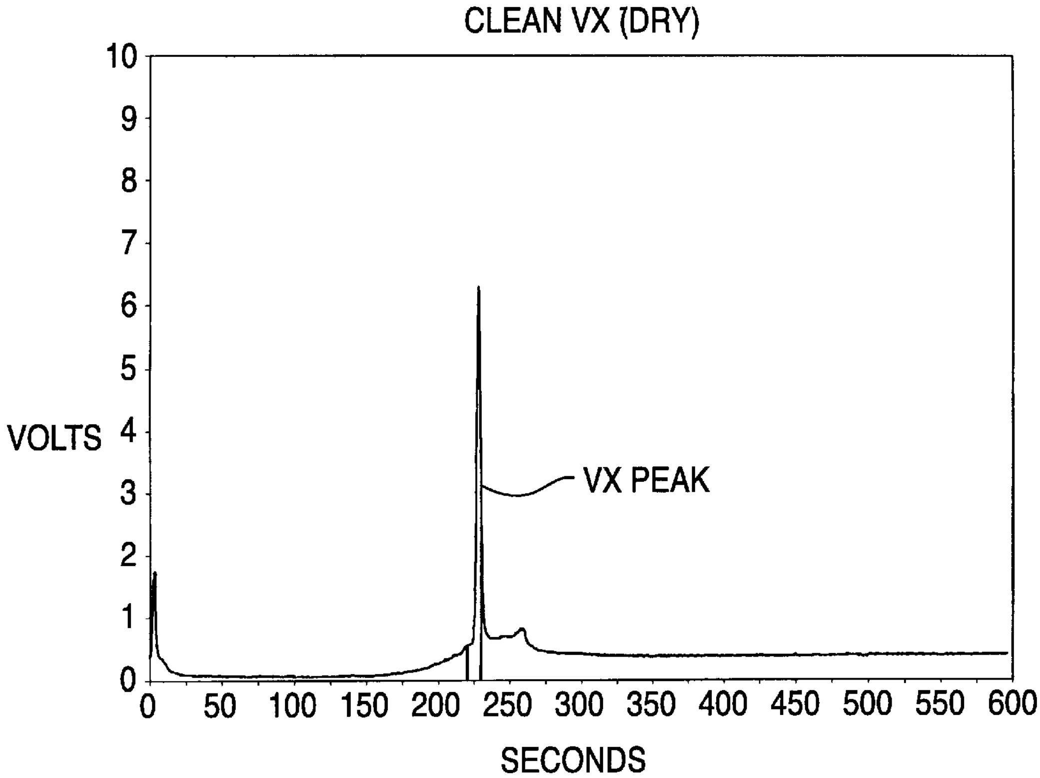

CLEAN VX (DRY)
VOLTS
0
1
2
3
4
5
6
7
8
9
10
VX PEAK
0
50
100
150
200
250
300
350
400
450
500
550
600
SECONDS

FIG. 5C

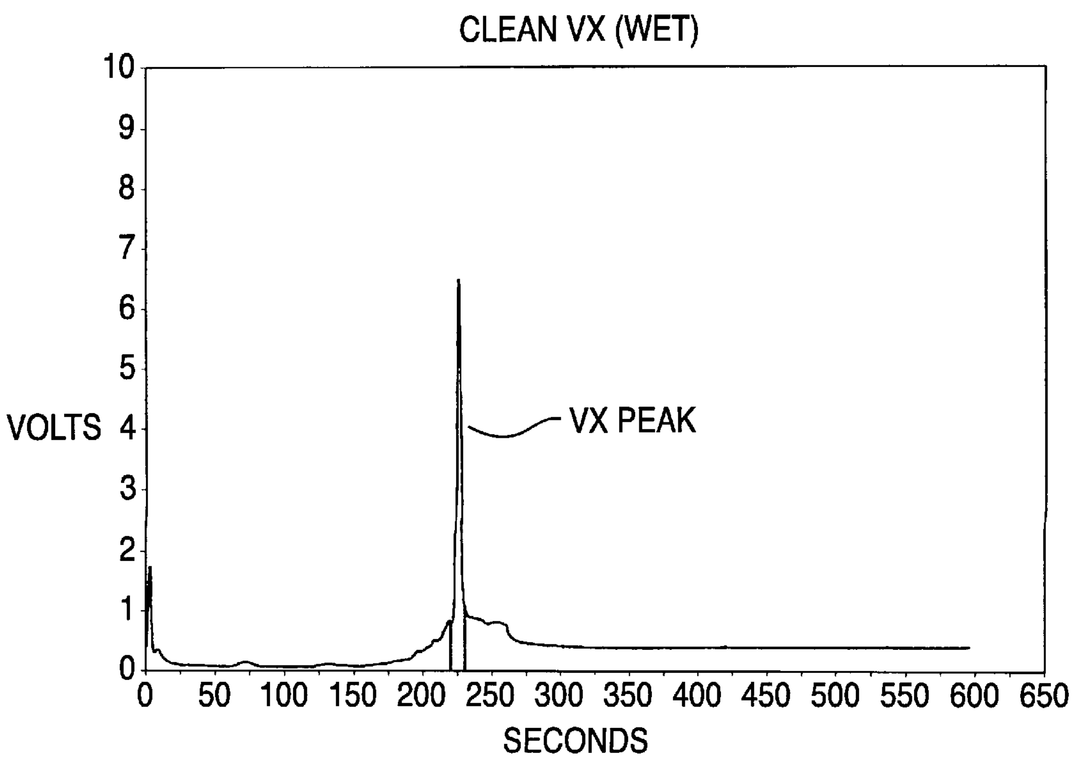

CLEAN VX (WET)
VOLTS
0
1
2
3
4
5
6
7
8
9
10
VX PEAK
0
50
100
150
200
250
300
350
400
450
500
550
600
650
SECONDS

FIG. 5D

ANALYTICAL METHODOLOGY FOR QUALITATIVE AND QUANTITATIVE DETERMINATION OF CHEMICAL AGENT VAPOR

GOVERNMENT INTEREST

The invention described herein may be manufactured, licensed, and used by or for the U.S. Government.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the qualitative and quantitative determination of chemical agents. More particularly, the present invention is a method for determining O-ethyl S-(2-diisopropylanimoethyl) methylphosphonothiolate, better known as VX, vapor. Most particularly, this invention permits the generation of a purer non-contaminated VX vapor and the analytical determination of the VX samples collected under various relative humidity conditions.

2. Brief Description of the Related Art

O-ethyl S-(2-diisopropylanimoethyl) methylphosphonothiolate, better known as VX, is an extremely toxic chemical warfare agent. It is a relatively stable compound that undergoes slow degradation. For example, the non-stabilized VX of 95% purity, without adding a compound stabilizer, decomposes at a rate of approximately 5% per month at 25° C. The decomposition impurities include ethyl methylphosphonic acid, methylphosphinic acid, diisopropylaminoethyl mercaptan, diethyl methylphosphonate, and ethanol.

As an extremely toxic compound, VX detection is best accomplished at the lowest possible concentration. Chemical detectors used for the detection of VX require calibration. Vapor samples of a known concentration of VX are used to test and evaluate these detectors. The VX samples need to be qualitatively pure and quantitatively analyzed to be useful in properly evaluating different chemical agent detectors.

Pure VX samples, of 95% or greater (CASARM quality), are useful in testing chemical agent detectors. CASARM (Chemical Agent Standard Analytical Reference Materiel) VX is used for instrument calibration to provide truest reference. Compound stabilizer is not added within the neat VX sample. However impurities within the VX sample itself, such as at approximately 5%, affect detector testing in a disproportionate manner. Volatility differences between VX and accompanying impurities within a sample produce vapors that are not representative of the respective amounts of VX and impurities within the liquid sample. Greater vaporization rates of the impurities produce a vapor saturated with impure vapors during the initial vaporization of the VX sample. Impurities contained in a VX sample which are more volatile than VX, interfere with most chemical detectors as well as most analytical methodologies. As the amount of impurities within the VX sample decreases, an increase in the reliability of the testing of chemical agent detectors occurs. For example, 95% pure VX samples, having impurities such as diisopropylaminoethyl mercaptan (thiolamine) at 5%, produce vapors containing less than 1% VX vapor and greater than 99% thiolamine vapor. As such, these impurities cause significant interference with testing most chemical detectors as well as most analytical methodologies. As discussed above, although an impurity may only exist in small percentage in the liquid VX sample, it may become the major constituent in the vapor mixture when

vaporized. For proper VX vapor evaluation of detection devices and analysis, elimination of non-VX impurities (such as thiolamine) is necessary.

Several methods have been used to quantify a VX vapor sample. The Shoenemann reaction determines VX concentration by converting the VX into a G-agent analog before reacting with indole and peroxide to produce a fluorescence reaction. However, the reaction is interfered with by the existence of excess thiolamine. The thiolamine interferes with precipitate filtration as well as affecting the fluorescence reading of the sample. Thus, thiolamine may cause fluorescence false readings that affect the actual VX vapor concentration.

The presence of thiolamine also affects the outcome of the enzymatic method of analysis, which was developed to substantially negate the thiolamine effect. The lengthy enzymatic method requires detailed knowledge in the use and maintenance of the complex equipment. The enzymatic method also results in the generation of significant amounts of waste solution, requiring extensive disposal procedures. Additionally, the enzyme method does not distinguish the effects from other impurities in the VX vapor sample, nor identify the relative abundance of the impurities present.

Analysis by a gas chromatographic method, using a solvent containing bubbler to collect a vapor sample, provides a separation identification of the impurity vapors from the VX vapors. The method draws and collects the vapor into a solvent, only a small portion of which (approximately 5 microliters of a 5 milliliter sample) is then injected into a gas chromatograph (GC) equipped with a flame photometric detector (FPD). The VX peak, separated from the impurity peaks, is used to determine the VX vapor concentration. Because of the injection limitations, the gas chromatographic method has limited detection capability of approximately 0.04 mg/m^3 of VX concentration or greater. The accuracy and reliability of the method are compromised from the combined affects of factors such as long sampling times of five to ten minutes, collection efficiency, solvent evaporation, and small sample injection. The method, although effective for analyzing VX vapor at low relative humidity conditions, is unable to analyze VX vapor sample collected under high humidity conditions. When used under high humidity conditions, the VX peak may be lost or substantially diminished from an expected concentration.

Also known in the art, VX vapor may be analyzed using the Miniaturized Continuous Air Monitoring System (MINICAMS), described in U.S. Pat. No. 5,014,541 (Sides et al.) and U.S. Pat. No. 5,052,805 (Sides), which issued on May 14, 1991 and Oct. 1, 1991, respectively. It provides a method of detecting VX vapor by passing the VX vapor through a conversion pad that converts the VX vapor into a more volatile G-analog similar to the conversion process of the fluorescence method, described above. Conversion efficiencies are affected by the age of the conversion pad, the temperature and humidity, the flow rate through the pad, impurities and other factors. The MINICAMS' FPD detector detects the converted G agent analog peak, thereby deriving an equivalent VX concentration. Such MINICAMS method is not useful for precise quantitative and qualitative analysis because of the quality of the conversion pads and the unknown effects from the associated impurity vapors. Additionally, such MINICAMS method lacks the ability to separate or distinguish the relationship between the impurities and VX.

In addition to low volatility, VX readily adheres to most surfaces contacted. As such, low concentrations of VX sample are significantly reduced when transferred through any additional tubing or connections. This reduction significantly interferes with conventional methods in quantifying VX agent vapors for testing chemical agent detectors.

In view of the foregoing, improvements in chemical monitoring have been desired. It has been desired to provide an improved methodology for sampling VX both quantitatively and qualitatively.

SUMMARY OF THE INVENTION

The present invention provides a method for generating and sampling chemical agent vapor comprising the steps of placing liquid chemical agent in a reservoir, maintaining the reservoir at a sufficient temperature to vaporize contaminants within the chemical agent; purging the contaminant vapor with dry air, wherein the dry air removes contaminant vapor from the reservoir while retaining the chemical agent in the reservoir, adjusting the temperature of the reservoir sufficient to form vapor from the retained chemical agent; flowing conditioned air over the vaporizing retained chemical agent, wherein conditioned air mixes with and carries the chemical agent vapors from the reservoir to a sample port; and, analyzing the mixture of conditioned air and chemical agent vapors at the sample port.

BRIEF DESCRIPTION OF DRAWINGS

FIG. **1** illustrates an agent generation system comprising a delta tube and MINICAMS chemical monitoring system;

FIG. **2**A is a GC chromatogram of a VX sample containing significant impurities;

FIG. **2**B is a MINICAMS chromatogram of a VX sample containing significant impurities;

FIG. **3**A is a GC chromatogram of a VX sample containing slight impurities;

FIG. **3**B is a MINICAMS chromatogram of a VX sample containing slight impurities;

FIG. **4**A is a GC chromatogram of a pure VX sample of the present invention;

FIG. **4**B is a MINICAMS chromatogram of a pure VX sample of the present invention;

FIG. **5**A is a MINICAMS chromatogram of a VX sample containing significant impurities under dry relative humidity conditions;

FIG. **5**B is a MINICAMS chromatogram of a VX sample containing significant impurities under wet relative humidity conditions;

FIG. **5**C is a MINICAMS chromatogram of a pure VX sample under dry relative humidity conditions of the present invention; and,

FIG. **5**D is a MINICAMS chromatogram of a pure VX sample under wet relative humidity conditions of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides a method for generating vapors from low volatility chemical compounds, such as Sarin (GB), Tabun (GA), Soman (GD), Distilled Sulfur Mustard (HD), Nitrogen Mustard (HN3), Lewisite (L), and O-ethyl S-(2-diisopropylanimoethyl) methylphosphonothiolate (VX) agent, and/or other like compounds, and sampling those vapors. Preferably, the present invention is a method for generating and sampling pure VX agent samples regardless of the humidity conditions. The methodology provides for the purification of VX agent sample within a delta tube, and later vapor analysis of that sample using a MINICAMS as the analytical instrument. A stream of dry air is swept over a small drop of liquid VX sample which contains thiolamine and other higher volatile impurities in the delta tube. The thiolamine and other higher volatile impurities are gradually purged. The purged VX sample becomes a pure or clean VX agent. The pure VX agent vapor is transferred directly from the delta tube into a manifold where it is mixed with a conditioned air at a specific relative humidity (RH) to form a targeted VX vapor concentration. The MINICAMS uses GC-FPD (Flame Photometric) detector for VX detection directly without the need to convert the VX into its more volatile G-analog.

As seen in FIG. **1**, a vapor generating apparatus **10** is shown having a delta shaped tube **20** which is used as the chemical agent reservoir. The vapor generating apparatus **10** generates a gas concentration to test chemical agent detectors. The generated gas sample is analyzed to provide a known concentration and purity for proper testing of the detectors.

A chemical agent **22** sample, in this case VX agent, is used in the vapor generating apparatus **10** The VX agent **22** sample usually contains small amounts of impurities. Preferably, the VX agent **22** sample has a high purity of 95% or greater VX agent **22**, more preferably from about 98% or greater VX agent **22**, and most preferably from about 99.5% or greater VX agent **22**. The VX agent **22** is placed into the delta tube **20**, and the delta tube **20** is then placed into a temperature bath **24**. The amount of the VX agent **22** sample may be any measurable amount which may be supported within the delta tube **20** while allowing the delta tube **20** to properly function. Preferably the sample amount of the liquid VX agent **22** is from about 10 microliters to 150 microliters, more preferably from about 10 microliters to 100 microliters, and most preferably from about 10 microliters to about 50 microliters. Smaller samples require shorter purging time to achieve clean VX. The delta tube **20** maintains the agent **22** at a constant temperature by immersion in the temperature bath **24**, which evaporates or vaporizes the impurities within the VX agent **22** in the delta tube **20** during a purging phase of the VX agent **22** sample. Additionally, the temperature bath **24** maintains the VX sample at a constant temperature to provide a stable vapor concentration for use during the detector testing phase.

During the purging phase, the temperature bath **24** is maintained at a temperature that permits the vaporization of impurities within the VX agent **22** sample without decomposing the VX agent **22**. Preferably during the purging phase, the temperature bath **24** is maintained at a temperature of from about 20° C. to about 100° C., more preferably from about 25° C. to about 75° C., and most preferably from about 35° C. to about 45° C. Vaporization is achieved while minimizing potential condensation at other parts of the apparatus during the process.

The constant temperature of the temperature bath **24** provides a constant vapor within the delta tube **20** resulting from the evaporation of the VX agent **22** sample. This vapor comprises gases from the VX agent **22**, as well as vapors from impurities within the agent **22**. The extremely low volatility of the VX agent **22** in comparison to the impurity components, provides a resultant vapor disproportionately comprised of vapors from the impurities in the VX agent **22** sample. As long as the low volatile VX agent **22** evaporates at a significantly slower rate than the impurities within the VX agent **22** sample, the vapors within the delta tube **20** will contain a significantly greater proportion of vapor from the impurities. VX agent **22** has a volatility that can be determined from the Antoine vapor pressure estimation using the formula log Pressure$_{(torr)}$=7.2810−[2072.1/(172.54+temperature$_{(degrees\ C)}$)]. Using the equation, VX at a temperature of 18° C. at one atmosphere has a volatility of approximately 3.72 mg/m^3. At 20° C., VX has a volatility of approximately 4.81 mg/m^3. At 25° C., VX has a volatility of approximately 8.86 mg/m^3. As the vapors are created in the delta tube **20** with the constant temperature of the temperature bath **24**, the delta tube **20** is also purged with air **12**. The more volatile impurities within the sample are purged from the sample at a greater rate than VX agent. After sufficient purge time, the impurities have been removed, and the sample comprises purified VX agent **22**.

The purification of the VX agent **22** provides a final purity of the agent **22** which is proportional to the flow rate, the initial purity of the starting sample, the temperature of the sample, and the type of impurities within the sample. The purge air **12** may be any dried carrier gas that permits the purging of the impurity vapors from the delta tube **20**. This includes, but is not limited to, atmospheric air, nitrogen, helium, and the like. The purge air **12** comprises a sufficiently low humidity and is sufficiently clean or filtered as to not contaminate the VX agent **22** within the sample during purging. The dry air **12** preferably has a moisture content of from about 5% or less, more preferably from about 2% or less, and most preferably from about 0.5% or less. The purge air **12** flow rate comprises any rate which permits efficient purging of the impurity vapors from the sample, preferably from about 20 cm^3/min to about 300 cm^3/min, more preferably from about 50 cm^3/min to about 250 cm^3/min, still more preferably from about 100 cm^3/min to about 200 cm^3/min, and most preferably from about 150 cm^3/min to about 175 cm^3/min. The duration or time of purge air **12** comprises any time period which efficiently purges the impurities from the sample, preferably from about 30 minutes to about 2 days, more preferably from about 2 hours to about 1 day, still more preferably from about 3 hours to about 12 hours, and most preferably from about 4 hours to about 5 hours.

After the VX agent **22** sample is purged, the VX agent **22** is heated to a temperature sufficient to create VX agent **22** vapors in the delta tube **20**. Conditioned air is flowed through the delta tube **20**, mixing with the VX agent **22** vapors and carrying the vapors out of the delta tube **20** reservoir to an outlet or sample port **16**. Conditioned air comprises air that is filtered, and adjusted to proper relative humidity conditions, which may be either high or low. The relative humidity of the conditioned air is varied by circulating the conditioned air through flowmeters **34**. Conditioned air may be any gas which does not interfere with the transfer of the VX agent **22** vapors to the sample port. Preferably, the conditioned air comprises an inert gas. More preferably, the conditioned air comprises nitrogen, argon, or helium. Most preferably, conditioned air comprises nitrogen.

Once the VX agent **22** sample is purged, and the vapor is mixed with conditioned air, the resultant vapor sample is collected into the pre-concentrator tube (PCT) of the Miniaturized Continuous Air Monitoring System (MINICAMS) **50** for concentration determination. As further seen in FIG. **1**, the MINICAMS **50** comprises a periodic monitoring system for the generated VX vapor. Although the MINICAMS **50** is a known type of chemical detection device, it is modified within the present invention to serve as an analytical instrument for samples collected from the vapor generating apparatus **10**. The MINICAMS **50** analyzes the VX agent **22** vapor flowing out of the vapor generating

apparatus **10**, providing a concentration value for the exiting vapors which is used to calibrate other chemical detectors.

Generally, the MINICAMS **50** is first calibrated with known samples of VX agent **22** to develop a calibration curve. The calibration curve is formed from plotted peak height values of respective chromatograms against the relative amount of VX to derive a standard calibration curve. Once plotted, the slope of the calibration curve is used to calculate the amount of VX agent **22** contained in the PCT sample collected from the vapor generating apparatus **10** to arrive at an equivalent vapor concentration. The chromatograms obtained from MINICAMS **50** on sequential samples are used to determine the relative purity of the VX agent **22** vapors derived from a given VX agent **22** sample within the delta tube **20** to monitor the purging progress.

The configuration of the MINICAMS **50** requires a sample vapor to pass through an inlet check valve and an inlet heater block before reaching the concentrating sorbent tube, known as PCT, **52**. Preferably, the sorbent of the PCT **52** is solid and has the ability to adsorb the sample vapor constituents. For low volatility compounds, such as VX agent **22**, substantial amounts of the vapor sample adhere to the valves and tubing before reaching the PCT **52** for subsequent desorption and analysis. The method of the present invention modifies the sampling routine of the MINICAMS by using a manual sampling technique to by-pass the inlet check valve and inlet heater block to collect the sample directly from the generating apparatus **10** into the PCT **52**.

This manual sampling technique requires disconnecting the PCT **52** from the MINICAMS **50** prior to collecting the VX agent **22** vapor. The PCT **52** is placed directly across the sample port **16** of the vapor generating apparatus **10**. A vacuum source draws on the opposite side of the PCT **52** from the sample port **16**, using such vacuum devices as a vacuum pump, suction ball or the like. The amount of suction may be any known amount that allows proper transfer of the VX agent **22** into the PCT **52**. Preferably the suction is from about 0.01 liters/minute to about 1.0 liters/minute, more preferably from about 0.05 liters/minute to about 0.5 liters/minute, and most preferably from about 0.1 liters/minute to about 0.3 liters/minute. The VX agent **22** within the air flow in the vapor generating apparatus **10** is drawn directly in and absorbed into the sorbent bed of the PCT **52**. The temperature of the PCT **52** is such as to allow the adsorption of the VX agent **22** into the PCT **52**. Preferably, the temperature of the PCT **52** is from about 0° C. to about 60° C., more preferably from about 20° C. to about 50° C., and most preferably from about 25° C. to about 35° C. By using the direct transfer of the present invention from the vapor generating apparatus **10** into the PCT **52**, VX agent **22** does not attach to tubing and/or other components within the MINICAMS **50**, which would contaminate the MINICAMS' inlet system and prevent the sample from reaching the sorbent material of the PCT **52**.

Once the agent **22** is transferred into the PCT **52**, the PCT **52** is re-inserted within the MINICAMS **50**. Once the PCT **52** containing the VX agent **22** is in the MINICAMS **50**, the VX agent **22** is purged for an additional period of time. A stream of zero air is passed through the sorbent in the PCT **52** which allows purging the trapped moisture when the VX agent **22** sample is collected in humid condition. The sorbent, by design, will retain the trapped VX and allow the moisture to evaporate. Generally, the zero air flows in a direction away from the gas chromatographic column within the MINICAMS **50** during its sampling cycle. Zero air comprises air which is clean and dry. Zero air includes any gas or gases known as air constituents, such as nitrogen, argon, helium, and other like inert gases, and combinations thereof. Preferably the zero air comprises an inert gas, and more preferably the zero air comprises nitrogen. Preferably, the zero air is filtered and dried atmospheric air. More preferably, the zero air has been filtered, dried, and chemically purified, and most preferably the gas is provided from a pure air generator. Additionally, preferably the zero air is dried to a relative humidity of from about 10% or less, more preferably from about 5% or less, and still more preferably from about 1% or less, and most preferably from about 0.5% or less. The time period of purging the PCT **52** containing the VX agent **22** in the MINICAMS **50** varies with the estimated moisture content. Preferably, zero air is swept across and purges the VX agent **22** for a time period of from about 30 seconds to about 300 seconds, more preferably from about 60 seconds to about 200 seconds, and most preferably from about 120 seconds to about 150 seconds.

After the zero air purges the moisture from the sorbent in the PCT **52**, the PCT **52** is heated and a suitable carrier gas, such as nitrogen, is swept across the PCT **52**. The carrier gas provides a carrier to the VX agent **22** vapor to flow into the gas chromatographic column as it eludes from the heated PCT **52**. Preferably the PCT **52** is heated to a temperature of from about 40° C. to about 250° C. for 215 seconds, more preferably from about 50° C. to about 250° C. for 210 seconds, and most preferably from about 60° C. to about 240° C. for 200 seconds. The carrier gas comprises any gas which permits the VX agent **22** to be carried into the gas chromatographic column and which does not interfere with the workings of the gas chromatographic column. Preferably, the carrier gas comprises nitrogen gas or helium gas. More preferably, the carrier gas comprises nitrogen gas. The flow rate of the carrier gas is fixed which permits proper elution of the VX agent **22** through the gas chromatographic column. Preferably, the flow rate of the carrier gas is regulated by the carrier gas pressure from 35 psi to 50 psi more preferably from about 40 psi to 45 psi, and most preferably from about 40 psi to 42 psi.

The VX agent **22** is separated from any impurities in the gas chromatographic column and is detected both qualitatively and quantitatively by the Flame Photometric Detector (FPD). The VX agent **22** is qualified by peak separation of the VX agent **22** from sample impurities within the gas chromatographic column. The gas chromatographic flame photometric detector (GC-FPD) within the MINICAMS derives the chromatogram. The VX agent **22** is quantified by measuring the VX agent **22** peak indicated in the gas chromatographic trace of the sample, from which a determinable amount of VX agent **22** may be calculated based on the calibration curve using known amounts of standard solutions.

The method of the present invention produces a gradual cleansing of the VX samples, and eventually achieves a highly purified VX stage that produces non-contaminated (highly purified) VX vapor. With the non-contaminated VX agent **22**, the present invention permits analytical calibration of the vapors generated within the vapor generating apparatus **10**. Once the generated vapor is calibrated, the correct testing and evaluation of VX vapor detectors **50** using the vapor generating apparatus **10** is possible.

After the vapor produced by the vapor generating apparatus **10** is calibrated, chemical agent detectors **50** are tested. As seen in FIG. **1**, the flow rate and humidity are controlled within the vapor generating apparatus **10** through solenoid assembly **14** to the detector sample port **16**. The VX agent **22** vapors may be diluted to the desired concentration and humidity conditions to provide proper realistic detector testing by the following process. The vapor generating apparatus **10** provides a chemical agent stream diluted to the desired concentration at controlled humidity condition. Additionally, a paralleled conditioning stream **18** of air without the chemical agent exists which has similarly controlled humidity condition as the chemical agent stream. The vapor generating apparatus **10** is regulated to provide the desired relative humidity and concentration. The concentration is proportional to the flow rate over the VX agent **22**, the flow rate of the mixing gases in a manifold **28**, and the temperature of the temperature bath **24**. Chemical agent detectors **50** are attached to the sample port **16** and tested for the given relative humidity and concentration conditions. After a series of chemical agent detectors **50** are tested or challenged, the relative humidity and concentration within the vapor generating apparatus **10** may be changed to provide testing for different concentrations and amounts of relative humidity. After the relative humidity and concentration are varied, the vapor generating apparatus **10** is re-calibrated by analyzing the VX agent **22** vapor sample once again with the method of the present invention, as previously described. During the chemical agent detector **50** testing phase, the detectors **50** and the portion of the apparatus **10** after the mixing manifolds **28**, may be placed in an environmental chamber **32** set at any temperature which permits testing of the chemical agent detectors **50** as required, which is an amount equivalent to the VX sample **22** vaporized within the delta tube **20**. Preferably, the chamber **32** temperature is from about −10° C. to about +52° C., more preferably from about 0° C. to about +45° C., and most preferably from about +20° C. to about +30° C. according to the test requirements.

FIGS. **2**A and **2**B show GC chromatograms of a VX sample for a freshly charged generator vapor sample. The chromatograms show significant impurities on the GC chromatograms where the impurities overwhelm the VX data. However, the GC chromatogram of FIG. **2**A shows the less volatile VX agent **22** coming off the column at a later time than the impurities within the sample. The impurities contain such compounds as thiolamine. Similarly, the MINICAMS chromatogram trace in FIG. **2**B shows the same impure VX sample, and also indicates a separate peak for VX agent, with the impurities interfering with the VX agent GC trace.

A VX agent **22** sample which has been purged for a period of time is shown in FIGS. **3**A and **3**B. FIG. **3**A shows a standard GC chromatogram of the VX sample containing slight impurities. The impurities do not interfere with the VX agent **22** trace as shown in FIGS. **2**A and **2**B. FIG. **3**B shows a MINICAMS chromatogram trace of a VX sample containing slight impurities similar to FIG. **3**A. The relatively clean VX agent **22** sample provides for a better qualitative and quantitative analysis of the VX agent **22** within the sample.

FIGS. **4**A and **4**B show the VX agent sample after an extended purging time period. The very clean VX agent within the sample contains minuscule amounts of impurities. FIG. **4**A shows a standard GC chromatogram trace of a pure VX sample. FIG. **4**B shows a MINICAMS chromatogram trace of the same pure VX sample.

FIGS. **5**A–**5**D show various VX agent **22** samples under dry and wet relative humidity conditions. As seen in FIG. **5**A, a MINICAMS chromatogram of a VX agent **22** sample containing significant impurities under dry relative humidity conditions is extremely cluttered, obscuring the VX peak. In FIG. **5**B, a MINICAMS chromatogram of a VX agent **22** sample containing significant impurities under wet relative humidity conditions also is extremely cluttered. However in FIG. **5**C, a MINICAMS chromatogram shows a pure VX agent **22** sample under dry relative humidity conditions. The sample shown in **5**C has undergone the method of the present invention. The VX agent **22** sample is clearly distinguishable, and easily qualified and quantified. Additionally, the MINICAMS chromatogram of a pure VX sample under wet relative humidity conditions shown in FIG. **5**D also has undergone the method of the present invention. FIG. **5**D shows readily identifiable VX agent **22** without interference from impurities within the sample.

In operation, the method of the present invention provides analysis of VX agent **22** in high relative humidity conditions. VX agent **22** vapor which is collected under high humidity conditions is dried by allowing additional drying time during the sampling cycle of the MINICAMS using the zero air after the manually collected sample in the PCT **52** is returned to the MINICAMS before the heat desorption begins. As seen in FIG. **5**D, the high relative humidity VX agent **22** sample shows a separation from the associated impurities, indicating an effective analytically method.

The method of the present invention allows detection of from about $1–2\times10^{-9}$ grams of VX agent **22** or less. The concentration of VX agent **22** vapor detectable varies depending on the sampling rate and time. For example, a sampling rate of 500 cc/min for 1 min that yield a peak height equivalent to 1×10^{-9} g would equate to a vapor concentration of 1×10^{-9} g/0.5 liter which equals to 2×10^{-3} mg/m^3. The method may also be used as verification of compound volatility at very low temperatures and for compounds that have very low volatility because if its direct sample deposit and relative sensitivity. The method is particularly useful in compounds having a great affinity to surface adsorption, such as VX agent **22**.

EXAMPLE 1

To generate the VX vapor sample, VX agent was placed into a delta tube, while ensuring the amount of VX liquid did not block the diameter of the tube. The delta tube was connected to a vapor generator, using the method described in U.S. Pat. No. 5,728,927 (Ong), which issued on Mar. 17, 1998, the disclosure of which is herein incorporated by reference. A MINICAMS' PCT was placed at the sample port of the vapor generator, and a vacuum source was connected to the opposite end of the PCT. A sample from the vapor generator was collected manually by running the vacuum source at a known flow rate over a recorded time period. Once the sample was collected, the PCT was placed into the MINICAMS for analysis of the vapor sample. A calibration curve was derived using a MINICAMS chemical agent detector as an analytical device. The calibration curve was done by plotting the chromatographic peak heights of various concentrations of known amount of VX agent samples against the relative amount of VX, shown in Tables 1 and 2 below. Table 1 shows a VX calibration curve using different amounts of VX agent in an alcoholic solution at a known concentration of 5.1 ng/μl. Once plotted, the slope of the calibration curve is useful to calculate the amount of VX agent contained in the sample collected from the vapor generator to arrive at an equivalent vapor concentration as shown in Table 2 and Example 2.

TABLE 1

Amount Deposited in PCT (microliter)	VX Standard Concentration (nanogram/microliter)	Total VX Dosage (nanogram)	VX Peak Height (units)
1	5.1	5.1	516
2	5.1	10.2	1090
3	5.1	15.3	1479
4	5.1	20.4	1935

Table 2 shows several VX vapor calibration of samples from the generator at different RH conditions using sampling flow rate of 500 cc/min for 30 seconds.

TABLE 2

AGENT Sample Volume Time × Rate (m^3)	Peak Height Units	Equivalent Agent (nanogram)	Derived Vapor Concentration (mg/m^3)
2.5×10^{-4}	1167	12	0.047 mg/m^3
2.5×10^{-4}	808	7.5	0.030 mg/m^3
2.5×10^{-4}	477	4	0.016 mg/m^3
2.5×10^{-4}	661	6	0.024 mg/m^3

EXAMPLE 2

0.1 ml of VX liquid, having a purity of greater than 95%, was placed into a delta tube, while ensuring the amount of VX liquid did not block the diameter of the tube. The delta tube was connected to a vapor generator, using the method described in U.S. Pat. No. 5,728,927 with the temperature bath at 18° C. The VX agent was swept at a flow rate of 40 cm^3/min after being purged. The air exited from the delta tube was mixed with 3.5 liters of conditioned air, yielding a total of 3.540 liters at the sample port. A MINICAMS' PCT was placed at the sample or outlet port of the vapor generator, and a vacuum source was connected to the opposite side of the PCT. A sample from the vapor generator was collected manually by running the vacuum pump at a flow rate of 0.5 liter/minute over a time period of 0.5 minutes. Once the 0.25 liter sample was collected, the PCT was placed into the MINICAMS for analysis. The chromatographic peak representing the amount of VX agent within the sample was referenced against the calibration curve of example 1, and the concentration of the VX agent was calculated to equal to 8.09 nanograms. By calculation, the amount of VX vapor exiting from the delta tube reservoir equaled to 114.55 nanograms. Previous calculations indicated that such amount represented a volatility of the VX sample of 2.86 mg/m^3 experimentally derived as compared to the theoretical calculated value of 3.73 mg/m^3. It showed that a sweeping efficiency at 40 cc/min over a small drop of VX through the delta tube was approximately 76.6%, demonstrating the reliability of the present invention.

It should be understood that the foregoing summary, detailed description, examples and drawings of the invention are not intended to be limiting, but are only exemplary of the inventive features which are defined in the claims.

What is claimed is:

1. A method for generating and sampling chemical agent vapor, comprising the steps of:

placing liquid chemical agent in a reservoir;

maintaining the reservoir at a sufficient temperature to vaporize contaminants within the chemical agent;

purging the contaminant vapor with dry air, wherein the dry air removes contaminant vapor from the reservoir while retaining the chemical agent in the reservoir;

adjusting the temperature of the reservoir sufficient to form vapor from the retained chemical agent;

flowing conditioned air over the vaporizing retained chemical agent, wherein conditioned air mixes with and carries the chemical agent vapors from the reservoir to a sample port;

analyzing the mixture of conditioned air and chemical agent vapors at the sample port, said analyzing comprising the further steps of:

providing a MINICAMS having removable PCT, wherein the PCT is separated from the MINICAMS;

transferring the mixture of conditioned air and chemical agent vapors into the PCT;

placing the PCT having the transferred chemical agent into the MINICAMS;

sweeping the transferred chemical agent in the PCT with zero air;

heating the PCT, wherein the chemical agent is desorbed;

flowing a carrier gas across the heated PCT, wherein the desorbing chemical agent is mixed with the carrier gas; and

measuring a chromatographic elution of the chemical agent within the carrier gas.

2. The method of claim **1**, wherein the chemical agent comprises a low volatility compound.

3. The method of claim **2**, wherein the chemical agent comprises a toxic chemical compound selected from the group consisting of Sarin (GB), Tabun (GA), Soman (GD), Distilled Sulfur Mustard (HD), Nitrogen Mustard (HN3), Lewisite (L), and VX agent.

4. The method of claim **3**, wherein the chemical compound comprises VX agent.

5. The method of claim **4**, wherein VX agent is from about 95% pure or greater when placed into the reservoir.

6. The method of claim **1**, wherein the reservoir containing the chemical agent is maintained at a constant temperature.

7. The method of claim **6**, wherein the constant temperature is from about 20° C. to about 100° C.

8. The method of claim **1**, wherein analyzing the mixture of conditioned air and chemical agent further comprises gas chromatography analysis.

9. The method of claim **1**, wherein flow rate of the purging dry air is from about 20 cm^3/min to about 300 cm^3/min.

10. The method of claim **1**, wherein the flow rate of the conditioned air is from about 20 cm^3/min to about 1000 cm^3/min.

11. The method of claim **1**, wherein the duration of the purging dry air is from about 30 minutes to about 2 days.

12. The method of claim **9**, wherein the step of analyzing the mixture comprises a sampling time of from about 5 seconds to about 30 minutes.

13. The method of claim **1**, further comprising the step of calibrating the MINICAMS.

14. The method of claim **1**, wherein the zero air has a relative humidity of from about 5% or less.

15. The method of claim **1**, wherein the flowing carrier gas comprises nitrogen.

16. The method of claim **1**, further comprising the step of testing a chemical detector with the analyzed mixture.

17. The method of claim **1**, further comprising the step of changing the relative humidity conditions prior to analyzing the mixture.

18. The method of claim **17**, further comprising the step of testing a chemical detector after changing the relative humidity conditions.

19. The method of claim **1**, further comprising the steps of determining vapor pressure and compound volatility measurements prior to maintaining the reservoir at a sufficient temperature to form vapor from contaminants.

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